Spirocyclic Anion Exchange Membranes for improved Performance and Durability

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May 19, 2020

DOE Hydrogen and Fuel Cells Program
2020 Annual Merit Review and Peer Evaluation Meeting

Project ID: FC178

Overview

Timeline and Budget

- Project start date: 01/01/18
- Project end date: 01/01/20
- Total project budget: $300k
  - Total recipient share: $0K
  - Total federal share: $300K
  - Total DOE funds spent: $300K

Barriers

- Cost
- Performance
- Durability

Partners

- NREL only project
- Multiple interactions across AEM space, leverage significant effort at NREL on related projects

Relevance/Impact
DOE (Preliminary) Milestones for AMFCs*

- **Q2, 2017:** Develop anion-exchange membranes with an area specific resistance ≤ 0.1 ohm cm^2, maintained for 500 hours during testing at 600 mA/cm^2 at T >60 ^oC.
- **Q4, 2017:** Demonstrate alkaline membrane fuel cell peak power performance > 600 mW/cm^2 on H_2/O_2 (maximum pressure of 1.5 atma) in MEA with a total loading of ≤ 0.125 mg_{PGM}/cm^2.
- **Q2, 2019:** Demonstrate alkaline membrane fuel cell initial performance of 0.6 V at 600 mA/cm^2 on H_2/air (maximum pressure of 1.5 atma) in MEA a total loading of < 0.1 mg_{PGM}/cm^2 , and less than 10% voltage degradation over 2,000 hour hold test at 600 mA/cm^2 at T>60 ^oC. Cell may be reconditioned during test to remove recoverable performance losses.
- **Q2, 2020:** Develop non-PGM catalysts demonstrating alkaline membrane fuel cell peak power performance > 600 mW/cm^2 under hydrogen/air (maximum pressure of 1.5 atma) in PGM-free MEA.

*taken from D. Papageorgopoulos presentation AMFC Workshop, Phoenix, AZ, April 1, 2016

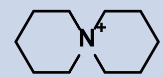
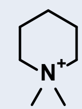
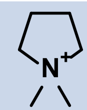
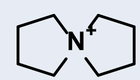
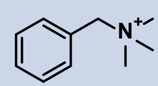
Relevance/Objectives

Alkaline exchange membranes continue to be challenged with cation degradation at high temperature and pH conditions

- State of the art trimethyl ammonium cations exhibit limited durability under fuel cell operating condition

- Research has indicated that cations with a spirocyclic structure have improved durability
    - Higher activation energy for both Hoffman elimination and substitution degradation mechanisms

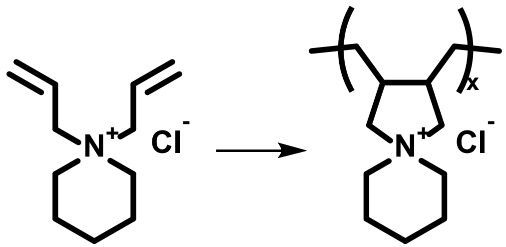
- Incorporation of spirocyclic ammonium cations into alkaline exchange membranes to improve durability

Quaternary Ammonium	Abbreviation	Half-life [hr]
	ASU	110
	DMP	87.3
	DMPy	37.1
	ASN	28.4
	BTMA	4.18

Marino, M. G.; Kreuer, K. D., Alkaline Stability of Quaternary Ammonium Cations for Alkaline Fuel Cell Membranes and Ionic Liquids. *ChemSusChem* **2015,** *8* (3), 513-523.

Approach

Synthesis
- Diallyl monomers undergo ring closing radical polymerization
- Polymerization of diallypiperidinium chloride produces repeat units that of an ASU/ASN hybrid structure



Polymer & copolymer characterization
- Structure
- IEC
- Conductivity

Accelerated aging
- Polymer & AEM durability
- Degradation pathways and rates

Leverage NRELs in-house expertise and MEA testing equipment

MEA fabrication and characterization
- Fuel cell performance
- Long term durability

- Previous work generated multiblock copolymers of polydiallylpiperidinium segments in a high performance polysulfone backbone
- Current synthesis focuses on scaling synthetic procedure for production of larger (>20 g) batches
  - Provide ample material for complete MEA characterization and durability studies

Approach - Milestones

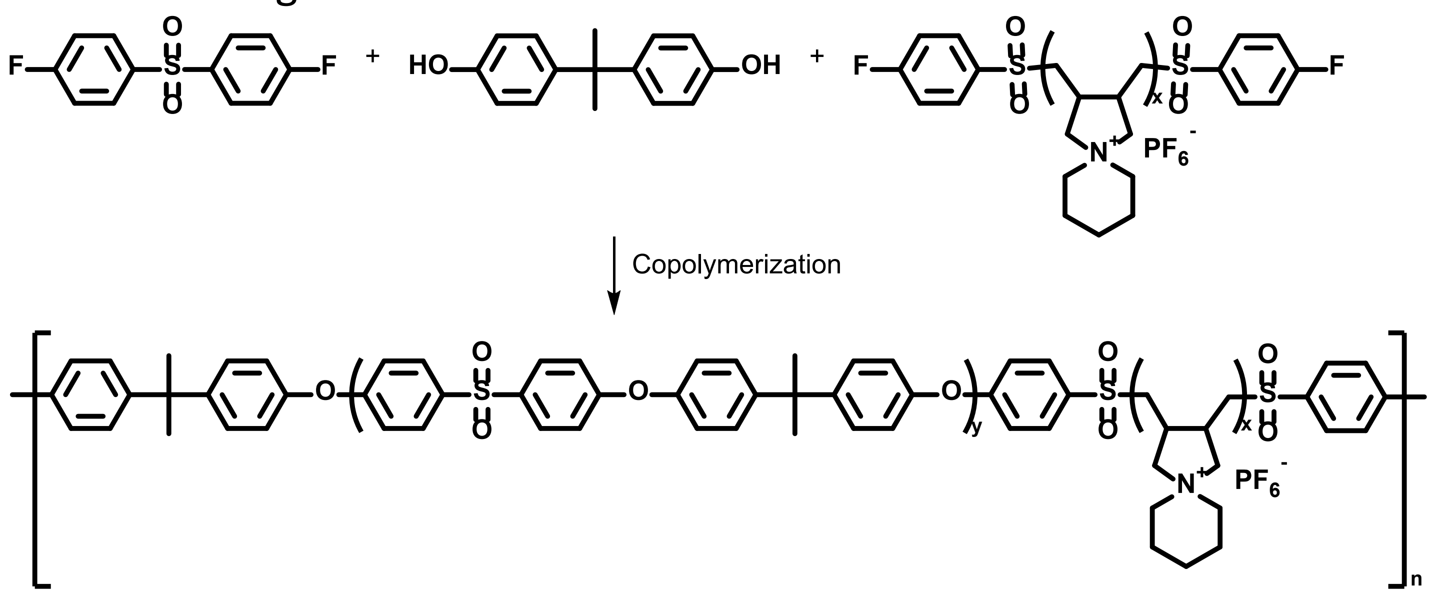
Milestone Name/Description	End Date	Type	Progress
In alignment with DOE 2019, Q2 AEM target, Demonstrate AEM fuel cell initial performance of 0.6 V at 600 mA/cm2 on H2/air (maximum pressure of 1.5 atma) in MEA, and less than 10% voltage degradation over 1,000 hour hold test at 600 mA/cm2 at T>60 oC.	12/31/2018	Progress Measure	Complete – 500 hours achieved
Develop ionomer solutions based on spirocyclic AEM polymers.	3/31/2019	Progress Measure	Complete
Quantify fuel cell performance of at least 3 different MEAs using spirocyclic ionomers and compare to baseline AMFC performance.	6/30/2019	Progress Measure	Complete
Optimize fuel cell performance based on a fully spirocyclic system where cathode and anode ionomer and membrane are spirocyclic based.	9/30/2019	Annual Milestone	Complete

Accomplishments and Progress

Synthesis

Polysulfone-PDApip multiblock copolymers

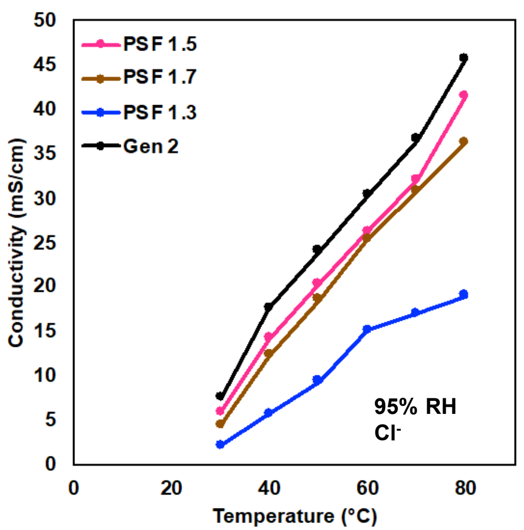
- Current polymerization method has produced material in as much as 16 g per batch
- Batch sizes are limited by the amount of spirocyclic homopolymer produced in an earlier step
- The spirocyclic homopolymer synthesis does not scale up efficiently, yields drop to ~20 % in ≥ 5 g batches

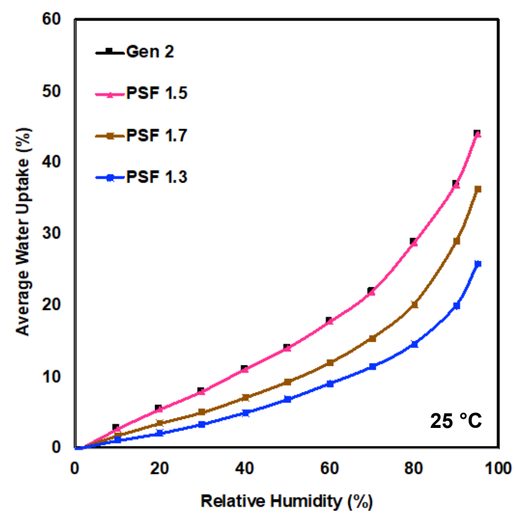


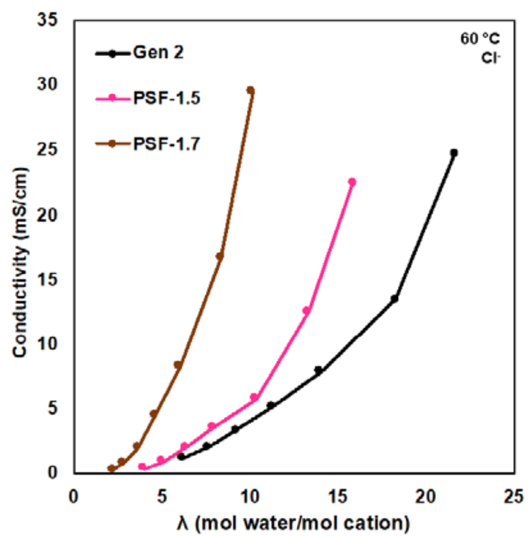
Accomplishments and Progress

Synthesis/Characterization

Polymer	IEC (measured) [mmol/g]	Cl^- Conductivity @RT in Water [mS/cm]	Water Uptake (%)	Peak Power Density (W/cm^2)
SpiroCyclic AEM	1.3	14.0	22	0.85
SpiroCyclic AEM	1.5	13.8	42	1.22
SpiroCyclic AEM	1.7	16.1	80	1.48
Gen 2 PF AEM	0.9	13.4	18	1.10



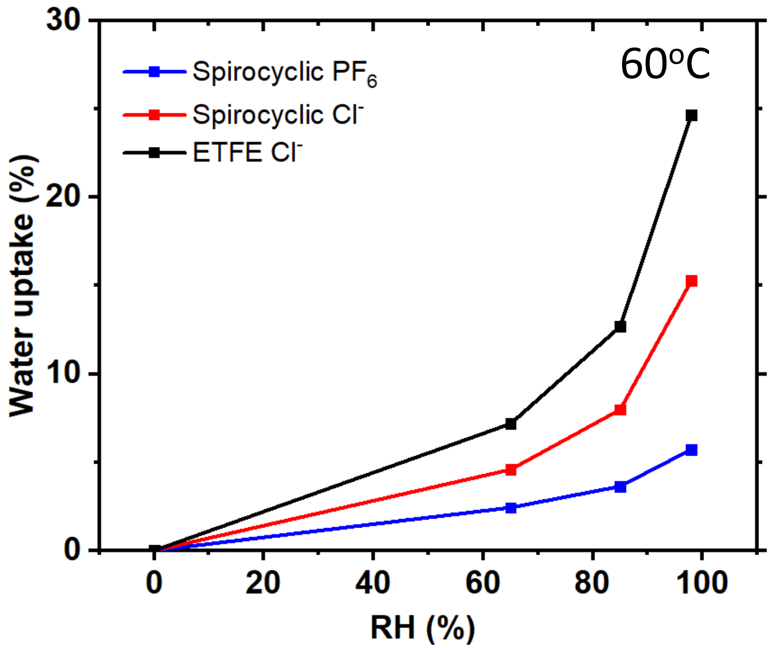


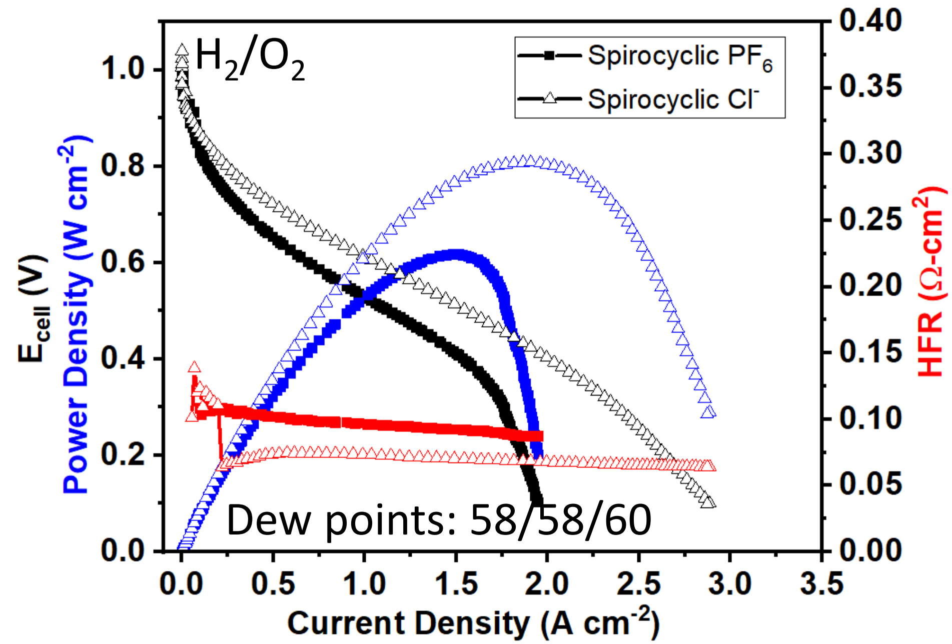


Accomplishments and Progress

Spirocyclic as Ionomer Incorporated into Electrodes

PF AEM Gen2 AEM, Spirocyclic ionomer (Cl^- form)



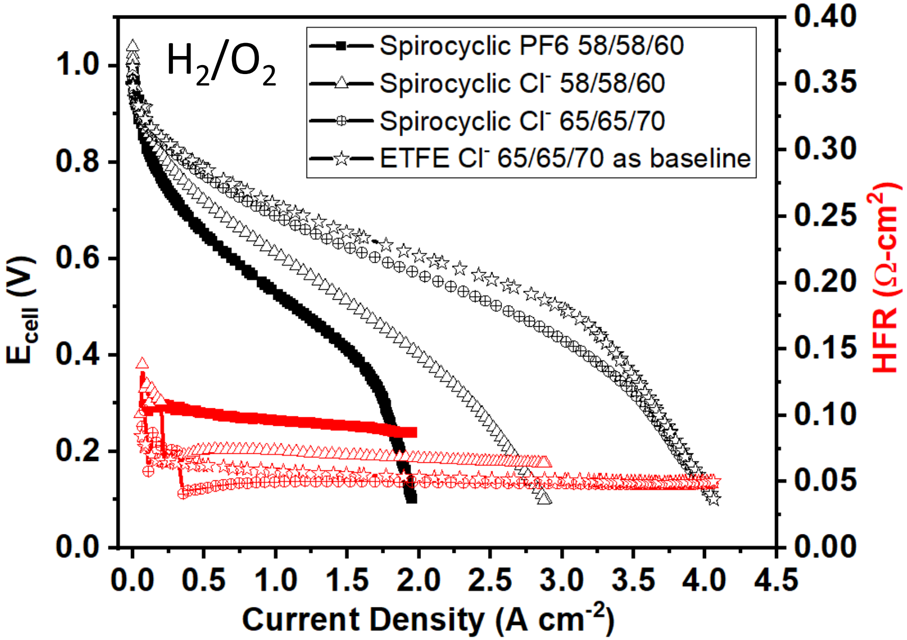


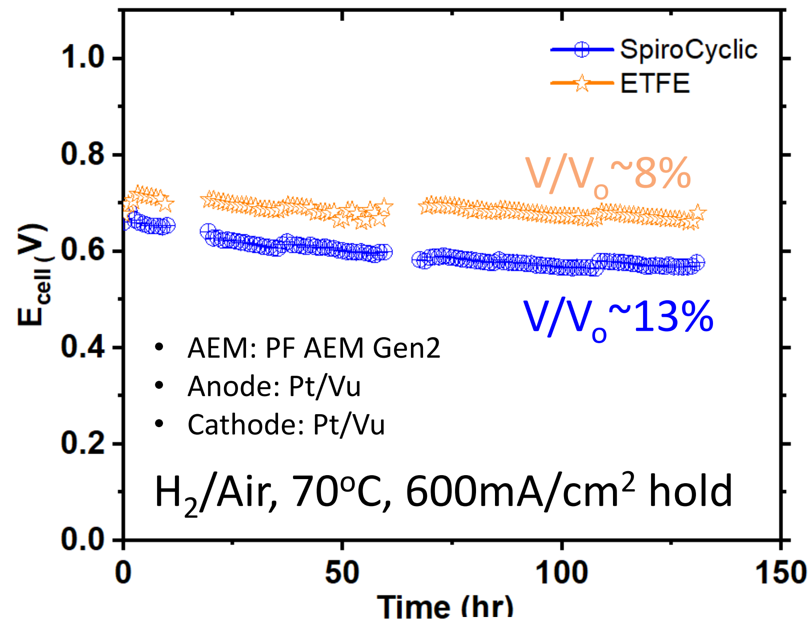
- Exchanging the spirocyclic ionomer in PF6 form to Cl- form to improve water transport in the electrodes layer
- Water uptake: ETFE > Spirocyclic Cl-> Spirocyclic PF6

- Significant improvement in fuel cell performance as well as obvious reduction in HFR
  - Ionomer: spirocyclic Cl-
  - Anode: 0.55 mg/cm^2 Pt/Vu
  - Cathode: 0.55 mg/cm^2 Pt/Vu
  - Membrane: Gen 2 PF AEM (50µm)

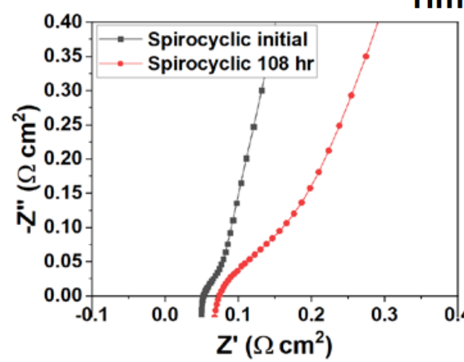
Accomplishments and Progress

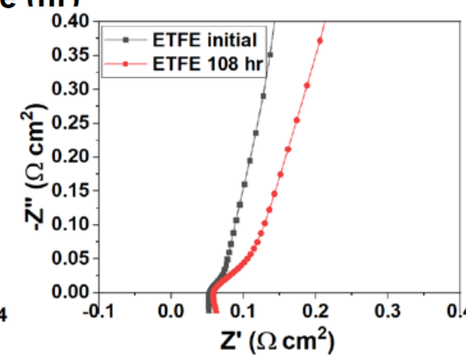
Three MEAs using spirocyclic as ionomer incorporated into electrodes





- PF AEM Gen2 AEMs were used in all the MEAs shown here
- Performance in Cl- > PF6 form (as shown in previous slide)
- Performance operating at 70°C is improved compared to operating at 60°C
- ETFE ionomer (baseline) with higher water uptake slightly outperforms spirocyclic ionomer MEA



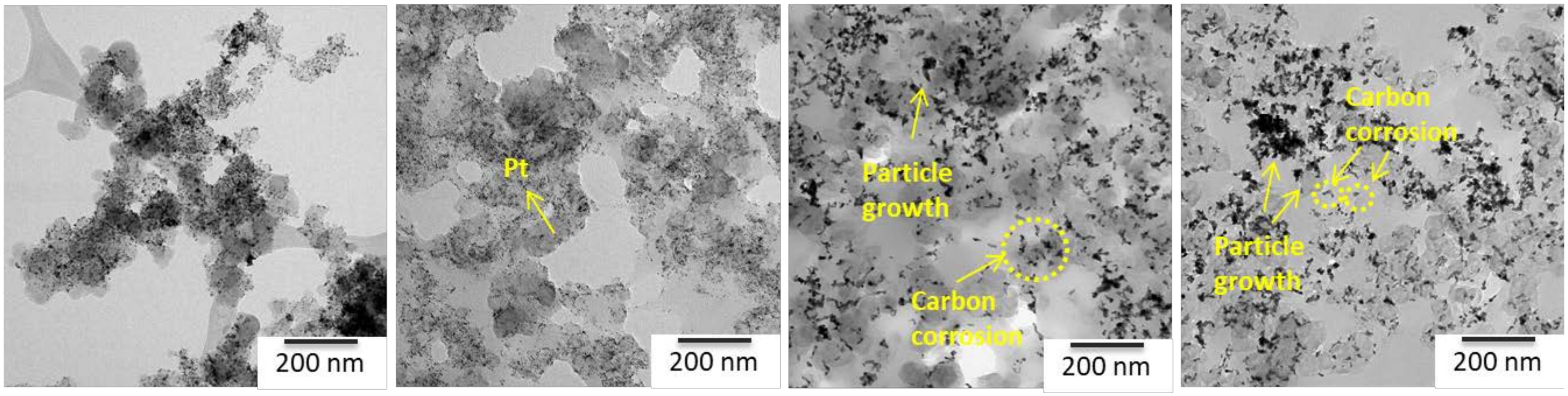


Full frequency impedance
H_2/N_2, 70°C, cathode

Accomplishments and Progress

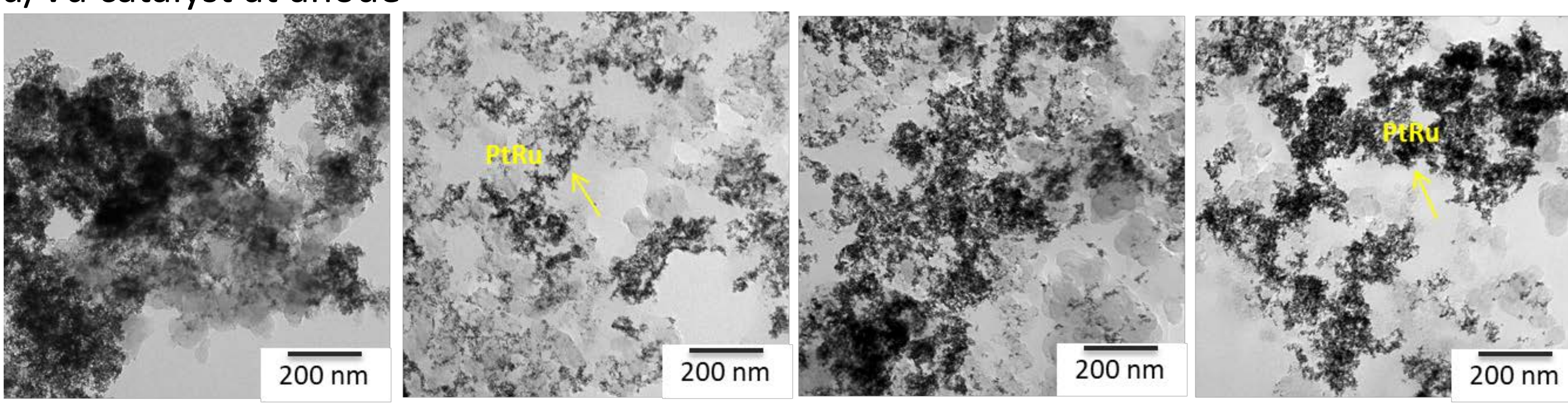
TEM characterization of electrode layers over the durability period

Pt/Vu catalyst at cathode | PSF-1.3$_{\text{pristine, 0 hr}}$ | PSF-1.7$_{\text{EOL, 150hr}}$ | PSF-1.3$_{\text{EOT, 550hr}}$



At cathode, obvious structural changes can be seen, e.g. pt particle growth and carbon corrosion over the testing period

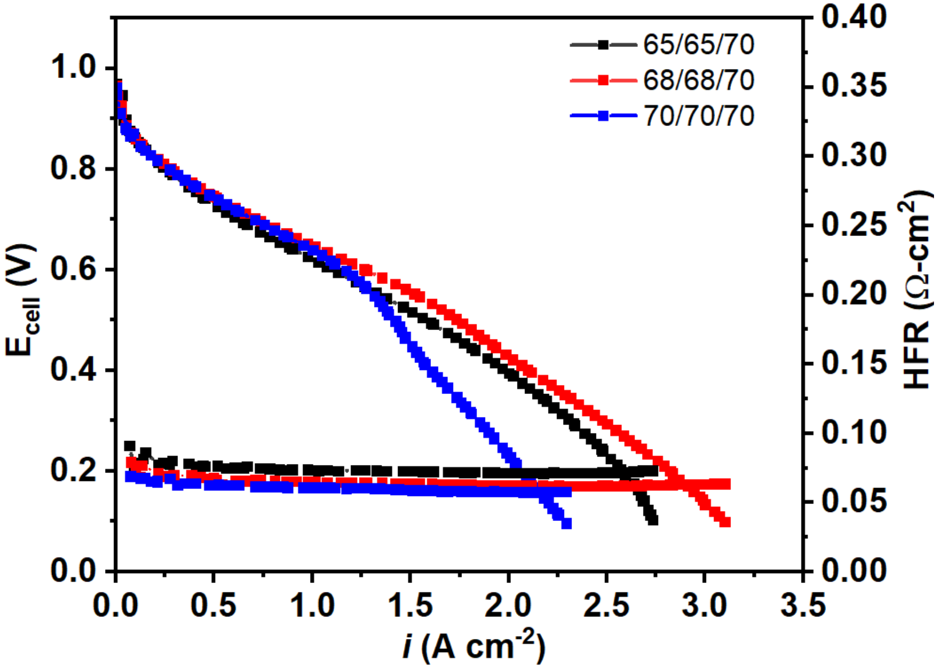
PtRu/Vu catalyst at anode

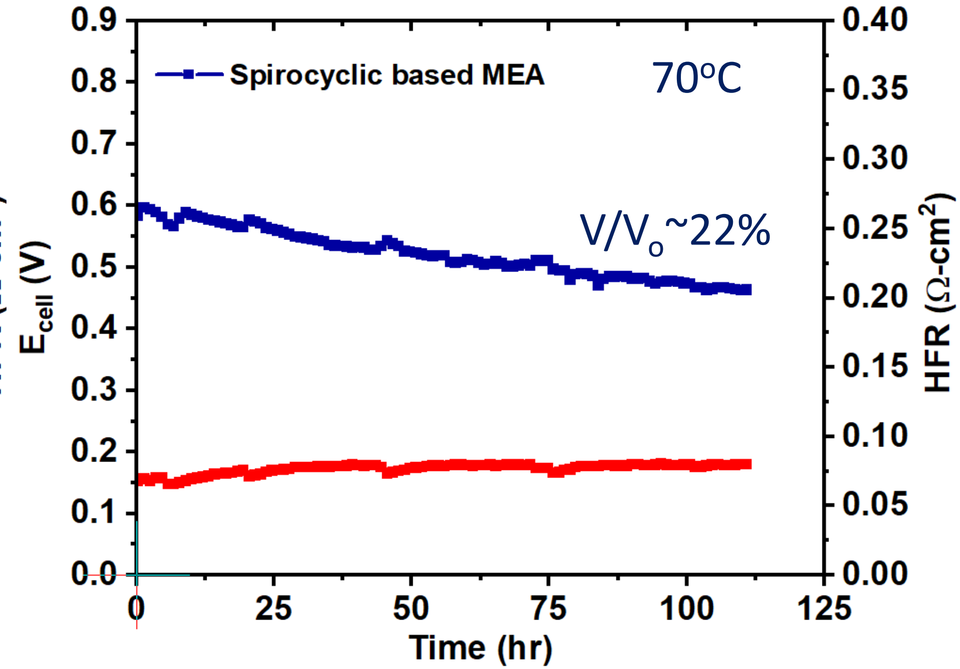


Unlike cathode, electrode structure remains similarly over the testing period at anode

Accomplishments and Progress

A complete spirocyclic system where cathode and anode ionomer, and membrane are spirocyclic based





<u>Membrane Electrode Assembly</u>

- AEM: Spirocyclic AEM 1.7 mmol/g
- Ionomer: spirocyclic Cl^-
- Anode: 0.55 mg Pt/Vu
- Cathode: 0.55 mg Pt/Vu

➢ A complete spirocyclic system was successfully assembled and tested with good initial performance

➢ Holding at 600mA/cm^2, degradation is > 20% in 115 hours. This is consistent with the previous result for the high-IEC spirocyclic AEM. In addition, higher operating temperature (70^{o}C) may also speed up the degradation of the membrane.

Collaborations and Coordinations

- NREL only (limited-funds) project that highly leverages significant effort at NREL on related projects including
  - PF AEM project
  - Membrane Working Group
  - ARPA-E efforts
  - FCTO HydroGEN AWSM (EMN) efforts

Summary

- We synthesized spirocyclic polymers of multiple ion exchange capacity (IEC)
- Lower IEC polymers were synthesized due to trends witnessed for increased durability with decreasing IEC.
- Thinner membranes were employed to limit the impact of lower IEC membranes in fuel cell tests.
- With optimized membranes greater than 500 hours of durability above 0.6V at 600 mA/cm2 was demonstrated.
- High performance with low total PGM loading was shown using spirocyclic membranes.
- Initial performance and durability of spirocyclic ionomer based electrodes showed promise.

Response to Reviewers comments: Project presented last year but not reviewed.

Remaining Challenges and Barriers/Future Work

Remaining Challenges and Barriers

Synthesis

- Large scale PDApip synthesis has poor yield
  - Limits the copolymerization scale

Accelerated aging characterization

- ^{1}H NMR unable to quantitatively assess the amount of degradation in PDApip polymers
  - Developing titration analytical method

Future Work

- Project is now complete